ORIGINAL ARTICLE

Determination of copper, nickel, manganese and cadmium ions in aqueous samples by flame atomic absorption spectrometry after simultaneous coprecipitation with Co(OH)$_2$

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Sayed Zia Mohammadi [a], **Tayebeh Shamspur** [b,*], **Yar Mohammad Baghelani** [a]

[a] *Department of Chemistry, Payame Noor University, Iran*
[b] *Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran*

Abstract A separation-preconcentration procedure was developed for the determination of trace amounts of copper, nickel, manganese and cadmium ions in water samples by flame atomic absorption spectrometry after coprecipitation by Co(OH)$_2$ as a carrier without a chelating agent. The influence of the various analytical parameters such as pH, amount of carrier reagent, standing time, centrifugation rate and time, sample volume and matrix effects on the recovery of the analyte ions was studied. Under the specified experimental conditions the calibration curves for Ni(II) and Cu(II) were linear from 0.5 to 200 ng mL^{-1} and for Mn(II) and Cd(II) from 0.5 to 250 and 0.3 to 80 ng mL^{-1}, respectively. The relative standard deviations for seven replicate determinations of a mixture of 40.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 20 ng mL^{-1} of Cd(II) in the original solution were 1.9%, 1.7%, 1.8% and 2.1%, respectively. The detection limits based on 3S$_b$/m for Cu(II), Ni(II), Mn(II) and Cd(II) in the original solution were 0.2, 0.2, 0.3 and 0.07 ng mL^{-1}, respectively. The limits of quantification based on 10S$_b$/m for Cu(II), Ni(II), Mn(II) and Cd(II) in the original solution were 6.7, 6.7, 10.0 and 2.3 ng mL^{-1}, respectively. The proposed method has been applied to the determination of trace amounts of the analyte ions in two certified reference materials (the National Institute for Environment Studies (NIES) No. 1 Pepperbush and NIES No. 7 Tea Leaves) and water samples and satisfactory results were obtained.

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* Corresponding author.
  E-mail address: shamspur@gmail.com (T. Shamspur).

1. Introduction

The monitoring of the levels of heavy metal ions in environmental samples is an important part of analytical chemistry due to their positive or negative influences on the human body (Hedberg et al., 2011; Mohammadi et al., 2011; Tobiasz et al.,

2012). Some metals such as manganese and copper are essential micronutrients and have a variety of biochemical functions in all living organisms. While these elements are essential, they can be toxic when taken in excess (Ensafi and Shiraz, 2008; Hedberg et al., 2011; Mohammadi et al., 2013a). However, some metals such as cadmium are non-essential metals as they are toxic, even in traces (Ensafi and Shiraz, 2008; Hajiaghababaei et al., 2013; Hedberg et al., 2011).

Atomic absorption spectrometer (AAS) is generally main instrument of analytical chemistry laboratories for the determination of traces heavy metal ions, due to its relatively low cost. However the main two problems for the determination of heavy metal ions by AAS are low levels of metal ions and interferic influences of main components of samples (Hassanien and Abou-El-Sherbini, 2006; Mohammadi et al., 2013b). In order to solve these important problems, various preconcentration/separation methods including liquid liquid extraction (Lemos et al., 2012; Mirzaei et al., 2011), hydride generation (Miravet et al., 2004), cloud point extraction (Mohammadi et al., 2013b), dispersive liquid liquid microextraction (Mohammadi et al., 2016) and solid phase extraction (Dadfarnia et al., 2007; Mohammadi et al., 2010; Sabermahani et al., 2013; Yacoub et al., 2013; Afzali et al., 2012a,b) were used. However, these procedures are labor intensive, time and reagent consuming, and require large volume of sample.

Coprecipitation is also one of the efficient separation/preconcentration techniques for traces of heavy metal ions (Bulut et al., 2010; Saracoglu et al., 2006; Tuzen and Soylak, 2009; Zhang et al., 2004). The coprecipitation technique has some advantages: simple, fast method and several analyte ions can be preconcentrated and separated from the matrix simultaneously. In the coprecipitation procedure, a precipitate is formed by combination of a carrier element and a suitable inorganic or organic ligand (Divrikli and Elci, 2002). Various carrier elements including copper, nickel, aluminum, erbium, magnesium, indium, and samarium have been used (Bulut et al., 2010; Divrikli and Elci, 2002; Doner and Ege, 2005; Saracoglu et al., 2006; Soylak and Tuzen, 2008; Zhang et al., 2004; Uluozlu et al., 2009, 2010).

Titanium and zirconium, molybdenum and their oxides, were separated by coprecipitation with cobalt (II) hydroxide for a final determination by X-ray fluorescence spectrometry (Wurzinger and Muller, 1977). In this study, a separation/preconcentration procedure using Co^{2+} for coprecipitation of copper, nickel, manganese and cadmium ions has been developed prior to flame atomic absorption spectrometry (FAAS) determination. The most important advantage of the proposed method include absence of the need for any chelating agent, simplicity, low cost, enhancement of sensitivity, rapid analysis time and high enrichment factor.

2. Materials and methods

2.1. Instrumentation

A SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with deuterium background correction and air–acetylene burner was used for absorbance measurements. Copper, nickel, manganese and cadmium hollow cathode lamps were used as light source at wavelengths of 324.8,

232.0, 279.5 and 228.8 nm, respectively. The instrumental parameters are listed in Table 1. The acetylene flow rate and burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements. A Centurion scientific centrifuge model 1020 D.E. (West Sussex, United Kingdom) was used to accelerate the phase separation.

2.2. Reagents and solutions

Deionized water was used throughout the experimental work. Standard solutions of copper ($0.5–200.0$ ng mL^{-1}), nickel ($0.5–200.0$ ng mL^{-1}), manganese ($0.5–250.0$ ng mL^{-1}) and cadmium ($0.3–80.0$ ng mL^{-1}) were prepared by diluting stock solutions of 1000.0 mg L^{-1} of these ions supplied by Merck (Darmstadt, Germany). The working reference solutions were prepared daily by stepwise dilution from stock solutions with deionized water. For preparation of blank solution 50 mL distilled water was given and the pH was adjusted to 11 by NaOH solution. The laboratory glassware was soaked overnight in a 1.4 mol L^{-1} HNO$_3$ solution. Before using, all of the glasswares were washed with deionized water and dried. Solutions of alkali metal salts (1% w/v) and various metal nitrate and acetate salts (0.1% w/v) were used to study the interference of anions and cations, respectively. HNO$_3$ and NaOH solutions were used for pH adjustments.

2.3. Coprecipitation procedure

The coprecipitation procedure was optimized with 50 mL of an aqueous solution containing 5.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 1.0 ng mL^{-1} of Cd(II) prior to its application to the real samples. First, the pH of solution was adjusted to 11.0 by NaOH solution. Then 1.25 mL of 1000 mg L^{-1} of Co(II) was poured into the centrifuge tube. After 10 min, the mixture was centrifuged at 4000 rpm for 5 min. The supernatant was removed and the precipitate was dissolved with 2.0 mL of 4 mol L^{-1} HNO$_3$. The final solution was aspirated directly into the FAAS for determination of the analyte ions.

2.4. Preparation of real samples

Two certified reference materials (CRMs) supplied by the National Institute for Environment Studies (NIES) No. 1 Pepperbush and NIES No. 7 Tea Leaves have been analyzed. Approximately 0.5 g of NIES No. 1 and 1.0 g of NIES No.

Table 1 The instrumental parameters for analyte metals determination.

Analyte ion	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Optimum working range of instrument (µg/mL)
Cu(II)	324.7	0.5	4.0	0.03–10
Ni(II)	232.0	0.2	4.0	0.1–20
Mn(II)	279.5	0.2	5.0	0.02–5
Cd(II)	228.8	0.5	4.0	0.02–3

7 were weighted accurately into two Teflon cup (individually) and dissolved in concentrated nitric acid (∼10 mL) with heating on a water bath at 80 °C for 120 min. The solution was cooled and 50 mL deionized water was added to it and filtered by using cellulose membrane of 0.45 μm pore size (Millipore). The filtrate (approximately 60 mL) was made to 100.0 mL with deionized water in a calibrated flask. An aliquot (50 mL) of the sample solution was taken individually, and the analyte ions were determined by the coprecipitation procedure.

Water samples were collected in acid leached polyethylene bottles. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered before analyses through a cellulose membrane of 0.45 μm pore size (Millipore).

3. Results and discussion

At first the precipitate of $Co(OH)_2$, insoluble in water, was formed in pH 11.0 and then the analyte ions were accumulated on the coprecipitant ($Co(OH)_2$) over various mechanisms surface adsorption, ion-exchange, surface precipitation, and occlusion (Soylak and Onal, 2006). The influence of the various analytical parameters such as pH, amount of carrier element, standing time, centrifugation rate and time, sample volume and matrix effects on the recovery of the analyte ions was examined. The optimizations were carried out on 50 mL of an aqueous solution containing 5.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 1.0 ng mL^{-1} of Cd(II). Each experiment was repeated four times and averaged values are given as the results.

3.1. Effects of pH

The pH of the sample solutions was adjusted in a range of 7–12 by using diluted NaOH and the coprecipitation procedure was applied to this solutions. As can be seen in Fig. 1, the absorbance of the analyte ions increased with increase in pH and the maximum absorbance for copper, nickel and manganese obtained at the pH range 10.5–12, whereas the maximum absorbance for cadmium was obtained at the pH range 10.5–11.5. After pH 11.5, the absorbance of Cd(II) decreased with increasing of pH. Therefore, pH 11 was selected as optimum pH in all subsequent works for separation and preconcentration of the analyte ions.

3.2. Effect of amount of carrier element

The influence of amount of carrier element is an essential consideration for efficient extraction in coprecipitation procedure. For investigating the influence of amount of Co^{2+} as a carrier element on the coprecipitation procedure performance, several experiments were performed by adding varying amounts of Co^{2+} from 0.0 to 3.0 mg. The rest of the experimental conditions were kept constant. The results showed that, the absorbance of the analyte ions increased and reach to quantitative value for the analyte ions at the range of 1.0–3.0 mg. Therefore, 1.25 mg Co^{2+} was selected in all subsequent works.

3.3. Effect of standing time, centrifugation rate and time

The standing time, centrifugation rate and time were also examined. For investigating the influence of the standing time, 1.25 mL of Co^{2+} 1000.0 mg L^{-1} was added into 50 mL of an aqueous solution containing 5.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 1.0 ng mL^{-1} of Cd(II). Then, the standing time was investigated in the range of 0–20 min. The results showed that after 8 min, quantitative recoveries were obtained. Therefore, 10 min was selected as optimum standing time for all subsequent experiments. The effect of the centrifugation speed on the extraction of the analyte ions was investigated in the range of 1000–5000 rpm for 5 min. The results showed that, the maximum extraction was obtained for the analyte ions at 4000 rpm. Therefore, all further studies were performed at 4000 rpm.

The effect of centrifugation time on the extraction of the analyte ions was tested in the range of 2–15 min at 4000 rpm. The results showed that maximum extraction was obtained for the analyte ions in the range of 4–15 min. Therefore, 5 min was selected as optimum centrifugation time for all subsequent experiments.

3.4. Effect of sample volume

The effect of sample volume is a very important parameter in coprecipitation procedure (Sun, 1993; Uluozlu et al., 2009). To this purpose, the influence of the sample volume on the coprecipitation efficiency of the analyte ions was examined. In order to explore the possibility of enriching analytes from natural water with a high preconcentration factor, a series of sample solutions, containing 250.0 ng of Cu(II), Ni(II), Mn(II) and
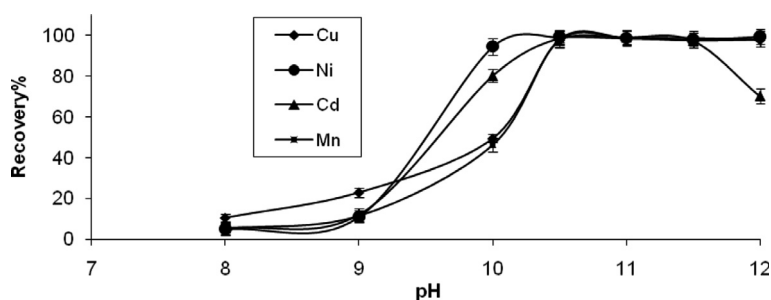

Figure 1 Effect of pH on the coprecipitation procedure, Conditions: sample volume, 50.0 mL, 5.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 1.0 ng mL^{-1} of Cd(II). Carrier element (Co(II)), 1.25 ml of 1000 mg L^{-1}; standing time, 10 min; centrifugation time, 5 min at 4000 rpm; final solution, 2.0 mL of 4 mol L^{-1} HNO$_3$.

Table 2 Tolerance limit of foreign ions.

Foreign ions	Interference/analyte ions(II) ratio[a]			
	Cu(II)	Ni(II)	Mn(II)	Cd(II)
$H_2PO_4^-$, HPO_4^{2-}	5000 ± 208	5000 ± 235	6000 ± 190	6000 ± 179
NO_3^-, CH_3COO^-, Na^+, K^+	7500 ± 30	5200 ± 83	6700 ± 28	6400 ± 34
SO_4^{2-}	>10,000	>10,000	>10,000	>10,000
Cl^-	>10,000	>10,000	>10,000	>10,000
Ca^{2+}	2500 ± 103	2500 ± 96	3000 ± 98	2500 ± 109
Mg^{2+}	3000 ± 121	3000 ± 128	2500 ± 114	2500 ± 110
Al^{3+}	500 ± 17	250 ± 9	250 ± 7	200 ± 6
Ag^+	500 ± 21	400 ± 12	400 ± 13	500 ± 18
Ba^{2+}	300 ± 10	300 ± 11	250 ± 6	300 ± 9
Cr^{3+}	500 ± 16	600 ± 19	500 ± 17	500 ± 15
Zn^{2+}	200 ± 8	150 ± 7	200 ± 7	200 ± 8
Fe^{3+}	200 ± 11	250 ± 12	200 ± 10	200 ± 6
Pb^{2+}	400 ± 21	500 ± 28	500 ± 18	400 ± 19

Conditions were the same as Fig. 1.

[a] Mean of four experiments, ±standard deviation.

Table 3 Analytical parameters of the method.

Statistical parameters	Cu	Ni	Mn	Cd
Linear ranges ($ng\,mL^{-1}$)	6.7–200.0	6.7–200.0	10.0–250.0	2.3–80.0
Regression equations	$A = 2.2173X + 0.0014$	$A = 2.8776X + 0.0015$	$A = 2.3969X + 0.0028$	$A = 8.5183X + 0.0039$
Correlation coefficient (R)	0.9992	0.9994	0.9998	0.9984
RSDa % (Intra-day, $n = 7$)	1.9	1.7	1.8	2.1
RSD % (Inter-day, $n = 7$)	2.1	1.9	2.2	2.6
Detection limit ($ng\,mL^{-1}$)	0.2	0.2	0.3	0.07

Conditions: Volume of the original solution, 50 mL, volume of the final solution, 2.0 mL, and other conditions were the same as Fig. 1.

Table 4 Determination of Cu(II), Ni(II), Mn(II) and Cd(II) in CRM samples.

Sample	Composition	Found[a] ($\mu g\,g^{-1}$)
NIES, No. 1 Pepperbush [b]	K, 1.51 ± 0.06, Mn, 0.203 ± 0.17, Ca, 1.38 ± 0.07, Mg, 0.408 ± 0.020%, Cd, 6.7 ± 0.5, Ni, 8.7 ± 0.6, Cu, 12 ± 1, Cs, 1.2, Tl, 0.13, Fe, 205 ± 17, Co, 23.0 ± 3, Pb, 5.5 ± 0.8, P, 1100, Cr, 1.3, Zn, 340 ± 20, Ba, 165 ± 10, Sr, 36 ± 4, As, 2.3 ± 0.3, Rb, 75 ± 4, Na, 106 ± 13, Hg, 0.05 $\mu g\,g^{-1}$	Cu: 12.2 ± 0.6 Ni: 8.6 ± 0.5 Cd: 6.8 ± 0.5
NIES, No. 7 Tea Leaves	Pb, 0.80, Cd, 0.030, Sb, 0.014, Zn, 33, Cr, 0.15, Al, 775, Mg, 1530, Ba, 5.7, K, 18,600, Sc, 0.011, Na, 15.5, Sr, 3.7, Ca, 3200, Cs, 0.22 l, Co, 0.12, Mn, 7.00, Ni, 6.5, Cu, 7.0 $\mu g\,g^{-1}$	Cu: 6.9 ± 0.3 Ni: 6.7 ± 0.5 Mn: 7.0 ± 0.3 Cd: 0.032 ± 0.003

[a] Mean ± confidence interval ($n = 3$).

[b] Concentration of Mn(II) is higher than linear range.

Cd(IfI) were studied in the volume range 20–600 mL at the optimum conditions. The results showed that the quantitative extractions were obtained for the analyte ions in the range of 20–500 mL. Therefore, 25 mL was selected as sample volume for all subsequent experiments. With respect to the final elution volume of 2.0 mL of HNO_3 and a breakthrough volume of 500 mL, a preconcentration factor of 250 was achievable.

3.5. Effect of foreign ion

Matrix effect is an important problem in the determination of heavy metals in the real samples. The effect of some important diver's ions on the absorbance of the analyte ions was also examined. For this study, 50 mL of an aqueous solution containing 5.0 $ng\,mL^{-1}$ of Cu(II), Ni(II), Mn(II) and 1.0 $ng\,mL^{-1}$ of Cd(II) was taken and different amounts of foreign ions were

Table 5 Determination of Cu(II), Ni(II), Mn(II) and Cd(II) in water samples.

Sample	Found[a] (ng mL^{-1})	Add values (ng mL^{-1})	Found (ng mL^{-1})	Recovery values after addition[a] (%)
Well water (Payame Noor University of Kerman)	Cu: 3.1 ± 0.1	Cu: 10.0	Cu: 13.3 ± 0.6	102.0 ± 0.9
	Ni: 7.4 ± 0.3	Ni: 10.0	Ni: 17.6 ± 0.8	102.0 ± 1.2
	Mn: 8.9 ± 0.4	Mn: 10.0	Mn: 19.3 ± 1.0	104.0 ± 0.4
	Cd: 2.31 ± 0.04	Cd: 10.00	Cd: 12.50 ± 0.04	101.9 ± 1.0
River Water (Rayen, Kerman)	Cu: 5.8 ± 0.3	Cu: 10.0	Cu: 15.5 ± 0.6	97.0 ± 0.4
	Ni: 6.5 ± 0.3	Ni: 10.0	Ni: 16.8 ± 0.7	103.0 ± 0.7
	Mn: 6.4 ± 0.4	Mn: 10.0	Mn: 16.2 ± 0.6	98.0 ± 0.2
	Cd: 1.08 ± 0.04	Cd: 10.00	Cd: 11.19 ± 0.04	101.1 ± 0.7
River Water (Shahdad, Kerman)	Cu: 7.9 ± 0.4	Cu: 10.0	Cu: 18.2 ± 0.7	103.0 ± 1.4
	Ni: 7.6 ± 0.3	Ni: 10.0	Ni: 17.5 ± 0.6	99.0 ± 0.9
	Mn: 7.1 ± 0.4	Mn: 10.0	Mn: 16.9 ± 0.6	98.0 ± 1.1
	Cd: 1.27 ± 0.06	Cd: 10.00	Cd: 11.17 ± 0.61	99.0 ± 0.3

[a] Average of four determination ± standard deviation.

Table 6 Comparison of the proposed coprecipitation procedure with other reported methods for preconcentration of the analyte ions.

System	Analysis method	Sample volume (mL)	RSD (%)	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	Refs.
Coprecipitation	FAAS	10	5%	–	Cu: 1.1	Saracoglu et al. (2003)
					Ni: 3.1	
					Mn: 1.0	
					Cd: 0.4	
Coprecipitation	FAAS	50	3.8%	250–5000	Cu: 1.3	Uluozlu et al. (2010)
Coprecipitation	FAAS	50	2–3%	–	Cu: 3.0	Doner and Ege (2005)
					Cd: 6.0	
Coprecipitation	FAAS	10	1–10%	–	Mn: 1.7	Soylak and Onal (2006)
Cloud point extraction	FAAS	15	Cu: 1.2	Cu: 10–250	Cu: 1.6	Ghaedi et al. (2008)
			Ni: 1.3	Ni: 10–200	Ni: 1.9	
Coprecipitation	FAAS	50	Cu: 1.9	Cu: 0.5–200.0	Cu: 0.2	Present work
			Ni: 1.7	Ni: 0.5–200.0	Ni: 0.2	
			Mn: 1.8	Mn: 0.5–250.0	Mn: 0.3	
			Cd: 1.1	Cd: 0.3–80.0	Cd: 0.07	

added to it and coprecipitation procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ±5% in the determination of Cu(II), Ni(II), Mn(II) and Cd(II) ions. The results are given in Table 2. The results showed that large numbers of anions and cations used have no considerable effect on the determination of Cu(II), Ni(II), Mn(II) and Cd(II) ions.

3.6. Calibration, precision and detection limits

Calibration curves were obtained by coprecipitation 50.0 mL of a sample solution containing of known amounts of four analyte ions under the optimized conditions. Enrichment factor was calculated as the ratio of the slope of calibration curve after and before of microextraction. The enrichment factors for Cu(II), Ni(II), Mn(II) and Cd(II) ions were 24.7, 22.7, 23.9 and 24.4, respectively. The reproducibility and the repeatability were evaluated with 50 mL of an aqueous solution containing 5.0 ng mL^{-1} of Cu(II), Ni(II), Mn(II) and 1.0 ng mL^{-1} of Cd(II). The repeatability (intra-day) and reproducibility (inter-day) of the method were evaluated by carrying out seven replicate extraction and determination of the analyte ions during a day (intra-day) and seven replicates at seven subsequent days (inter-day). The results were reported in Table 3. The detection limits based on 3S$_b$/m for Cu(II), Ni(II), Mn(II) and Cd(II) in the original solution were 0.2, 0.2, 0.3 and 0.07 ng mL^{-1}, respectively. Analytical parameters of the method are given in Table 3.

3.7. Accuracy of the method

The accuracy and applicability of the proposed coprecipitation procedure has been applied to the determination of Cu(II), Ni(II), Mn(II) and Cd(II) ions in National Institute for Environment Studies (NIES) No. 1 Pepperbush and NIES No. 7 Tea Leaves. Results are given in Table 4. It was found that there is no significant difference between results obtained by the coprecipitation procedure and the certified results. These results indicate the applicability of the coprecipitation procedure for copper, nickel, manganese and cadmium determination is free of interference.

3.8. Applications

The proposed coprecipitation procedure has been also applied to different natural waters for the enrichment and separation of the analyte ions. The results are given in Table 5. The utility of the coprecipitation procedure was also evaluated by examining the recoveries of the analyte ions from water samples spiked with the standard analytes. According to this Table, the added Cu(II), Ni(II), Mn(II) and Cd(II) ions can be quantitatively recovered from the water samples by the coprecipitation procedure. These results demonstrate the applicability of the procedure for copper, nickel, manganese and cadmium ions determination in water samples. The recovery of copper, nickel, manganese and cadmium added to the samples demonstrates the efficiency of the proposed procedure.

3.9. Comparison of the proposed method with the other methods

A comparison of the proposed coprecipitation procedure with the other reported preconcentration methods (Saracoglu et al., 2003; Uluozlu et al., 2010; Doner and Ege, 2005; Soylak and Onal, 2006; Ghaedi et al., 2008) for the copper, nickel, manganese and cadmium extraction from water samples are given in Table 6. The obtained detection limits, RSD% and linear range by the coprecipitation procedure are comparable or better than most of those reported in the literature.

4. Conclusions

The coprecipitation with cobalt hydroxide system without chelating agent offers a useful multielement preconcentration technique in environmental samples. The main benefits of the coprecipitation procedure were as follows: simplicity, low cost, enhancement of sensitivity, rapid analysis time and high enrichment factor. Also, the coprecipitation procedure does not need any chelating agent.

Acknowledgments

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